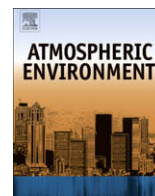




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## Large emissions of sesquiterpenes and methyl chavicol quantified from branch enclosure measurements

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### ABSTRACT

Multiple field studies have suggested chemistry within a forest canopy is poorly understood due to inadequate detection and quantification of reactive biogenic emissions, such as terpenes. To measure emission rates of terpenes at Blodgett Forest, a coniferous forest in the Sierra Nevada mountains of California, we placed enclosures over branches of the dominant species at the site – Ponderosa pine, manzanita, and ceanothus – in the summer of 2005. Zero air, with ambient CO<sub>2</sub> concentrations, flowed through the chamber system and volatile organic compound (VOC) emission measurements were made by proton transfer reaction mass spectrometry (PTR-MS), solid phase microextraction (SPME) on fibers followed by direct injection into a gas chromatograph with an ion trap mass spectrometer (GC-ITMS), and by in situ GC with a flame ionization detector (GC-FID). We show that previously undetected sesquiterpenes and methyl chavicol significantly contribute to the total reactive biogenic emission profile from this field site.

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### 1. Introduction

Biogenic volatile organic compounds (BVOCs) including terpenes (monoterpenes (C<sub>10</sub>H<sub>16</sub>) and sesquiterpenes (C<sub>15</sub>H<sub>24</sub>)) and the oxygenated aromatic methyl chavicol (C<sub>10</sub>H<sub>12</sub>O) are important for atmospheric chemistry because they contribute to secondary organic aerosol (SOA) production and play an important role in the oxidative capacity of the atmosphere (Andreae and Crutzen, 1997; Fuentes et al., 2000). Evidence of particulate formation or growth resulting from terpene oxidation products has been seen in forest ecosystems. Monoterpene oxidation products have been observed in both gas and particle phases in multiple forest ecosystems (e.g. Yu et al., 1999), and new particle formation in forests is most likely due to coagulation or condensation of terpene oxidation products (O'Dowd

et al., 2002). In a California Ponderosa pine forest downwind from Sacramento, terpene and isoprene oxidation products make up a significant fraction of the organic aerosol mass (Cahill et al., 2006), and fine particle growth events have been observed (Lunden et al., 2006). Bonn and Moortgat (2003) suggest that new particle formation in rural areas is most likely initiated by reactions of sesquiterpenes and ozone. Photooxidation of sesquiterpenes results in a greater aerosol yield than monoterpenes (e.g. Griffin et al., 1999) and photooxidation of methyl chavicol produced the highest SOA yield (40%) of all oxygenated compounds tested (Lee et al., 2006b).

Because terpenes are readily oxidized by O<sub>3</sub>, OH, and NO<sub>3</sub>, their short lifetimes range from minutes to hours (Atkinson and Arey, 2003). Several field experiments have provided indirect evidence of terpene oxidation. In a Michigan deciduous forest, Di Carlo et al. (2004) concluded that terpenes are likely responsible for the missing OH reactivity because it is temperature dependent. In the California Ponderosa pine plantation, chemical ozone loss due to reactions with BVOCs increased exponentially with

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temperature, suggesting that the ozone loss is mainly due to reaction with terpene-like compounds (Kurpius and Goldstein, 2003); these compounds are approximately 10 times the measured monoterpene flux (Goldstein et al., 2004). In a subsequent study, terpene oxidation products were observed above the forest (Holzinger et al., 2005) and confirmed by laboratory chamber experiments (Lee et al., 2006a,b).

All of these field studies suggest an inadequate detection and quantification of primary terpene emissions, particularly sesquiterpenes. Typical above canopy techniques are unable to detect the highly reactive terpenes. For example, Ciccioli et al. (1999) showed that  $\beta$ -caryophyllene is too reactive to escape an orange orchard canopy in Spain. Using a canopy model, Stroud et al. (2005) estimated that only 30% of  $\beta$ -caryophyllene would escape the canopy, as opposed to 90% of  $\alpha$ - or  $\beta$ -pinene. Primary emissions of highly reactive compounds are better measured using branch enclosures (Ortega and Helmig, 2008); the enclosures allow for the control of oxidant levels which would destroy highly reactive BVOC emissions while the branch remains as close to natural conditions as possible.

In this study conducted from July to September 2005, we investigate direct emissions from the major plant species at Blodgett forest in order to determine the emission rates of terpene-like compounds. Using multiple methods, we show sesquiterpene and methyl chavicol emissions can at times dominate the total terpene + methyl chavicol emission from the branches, contrary to previous studies.

## 2. Experimental

### 2.1. Site

This study was conducted at the Blodgett forest Ameriflux site, a Ponderosa pine (Ppine) plantation owned by Sierra Pacific Industries, located on the western slope of the Sierra Nevada mountains of California (38.90°N, 120.63°W, and 1315 m elevation). In the summer of 2005 the average tree height was 6.5 m. Mixing ratios and fluxes of CO<sub>2</sub>, H<sub>2</sub>O, and O<sub>3</sub>, along with meteorological parameters, have been measured at this site since 1997, and are reported in detail elsewhere (e.g. Goldstein et al., 2000; Bauer et al., 2000). In 2005, terpene emissions were determined by enclosing branches of the dominant tree, Ppine (*Pinus ponderosa* L.), and shrub species manzanita (*Arctostaphylos* spp.) and whitethorn ceanothus (*Ceanothus cordulatus*). Three Ppine branches from three different trees, and one branch from each of the shrub species, were sampled multiple times throughout the summer to assess seasonal differences in emissions. The sampling timeline is summarized in Fig. 1.

### 2.2. Branch enclosure system

The measurement chamber was made of heat-sealed 0.051 mm thick PTFE film (Richmond Aircraft Products) and placed directly over the branch (Fig. 2). The enclosure was fashioned to fit each individual branch and all heat-sealed edges were reinforced with PTFE tape (Scotch, 3M). To eliminate contamination from BVOCs in ambient air, dry

zero air from a zero air generator, supplemented with ambient CO<sub>2</sub> concentrations, flowed through the chamber system. With a  $\sim 4$  L min<sup>-1</sup> flow, the enclosure had a typical residence time of 20 s.

Prior to measurement, each branch was placed in the enclosure with ambient air-flow ( $\sim 10$  L min<sup>-1</sup>) for two full days to minimize the effect of emissions due to disturbance. Each branch was sampled for one day. It was also periodically shaded with aluminum foil to investigate light and temperature dependencies of primary emissions. Healthy Ppine branches were chosen  $\sim 3$  m above the ground, near the bottom of the canopy, and measurements were made on the most recent two years of needle growth. Healthy manzanita and ceanothus branches were chosen from a relatively undisturbed area in the forest. Branches were harvested on September 10, 2005, and the leaves or needles were removed, dried, and weighed in order to normalize the emissions from each branch by mass. Tubing ( $\sim 15$  m length) for the in situ gas phase instruments extended from the chamber sampling ports into a temperature-controlled container where the analytical instrumentation was housed.

### 2.3. Measurements

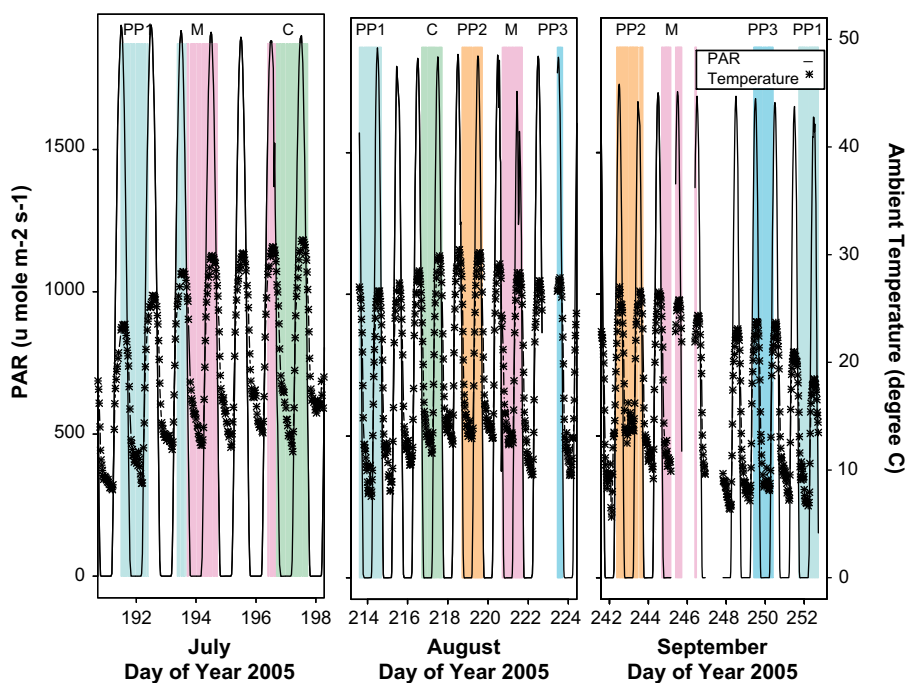
Water vapor, CO<sub>2</sub> (LI-6262, Licor Environmental), photosynthetically active radiation (PAR, LI-I90 Quantum Sensor, Licor Environmental), and air temperature inside the enclosure (thermocouples, Omega Engineering, Inc.) were measured continuously throughout the experiment.

BVOC emission measurements were made by proton transfer reaction mass spectrometry (PTR-MS), in situ gas chromatography with a flame ionization detector (GC-FID), and by solid phase microextraction (SPME) on fibers followed by direct injection into a gas chromatograph with an ion trap mass spectrometer (GC-ITMS). The GC-FID measured speciated monoterpenes while the PTR-MS focused on measuring total monoterpenes ( $m/z$  81 +  $m/z$  137), total sesquiterpenes ( $m/z$  205), and methyl chavicol ( $m/z$  149). The SPME fibers (Supelco) were used to measure speciated sesquiterpenes and methyl chavicol (Bouvier-Brown et al., 2007).

#### 2.3.1. PTR-MS

A wide range of VOCs were measured using a PTR-MS (Ionicon Analytik, Innsbruck); this instrument is described in detail elsewhere (Lindinger et al., 1998). BVOCs were identified by parent mass and correlation with the chromatographic techniques. Three times per day, the instrument sampled the zero air-flow entering the chamber to assess the background concentrations in the air supply.

**2.3.1.1. Calibration.** Standards were added periodically to the sample stream to correct for MS drift, transmission efficiency, and to check the concentrations calculated from the proton transfer reaction alone. One standard cylinder, containing compounds at concentrations of  $\sim 100$  ppb evenly distributed over the entire mass range ( $m/z$  33–219), was used routinely to determine the transmission curve of the quadrupole mass spectrometer. With this knowledge,



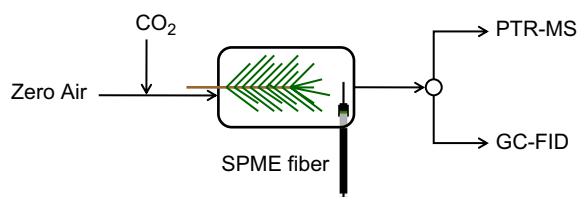
**Fig. 1.** Sampling timeline for summer 2005. The branch initials (PP1: Ponderosa pine branch #1, M: Manzanita, C: Ceanothus, PP2: Ponderosa pine branch #2, and PP3: Ponderosa pine branch #3) are indicated above the shaded region that corresponds to each sampling period. PAR and ambient temperature are indicated for the 3-month period. Heavy rain fell one month prior to measuring PP1 (June 16–18, day of year 167–169), but no rain occurred during the measurement period.

concentrations of unidentified compounds can be calculated with accuracy of  $\pm 30\%$  (Holzinger et al., 2005). The transmission curve is then checked with additional standards (Scott Marin, Inc. and Apel & Riemer), most of which contain a few ppm of one or more of the dominant monoterpenes found at the field site ( $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, and limonene). When calibrated with standards, the PTR-MS accuracy should be better than  $\pm 20\%$  (Holzinger et al., 2005). An additional calibration factor was determined for total sesquiterpenes using pure terpene standards.  $\alpha$ -humulene,  $\beta$ -caryophyllene, aromadendrene, longifolene,  $\beta$ -pinene,  $\alpha$ -pinene, limonene, 3-carene, and methyl chavicol (also known as 4-allylanisole or estragole) (Sigma–Aldrich or Fluka Chemicals through Sigma–Aldrich) were diluted in cyclohexane. After filling a 10 L Tedlar bag (SKC, Inc.) with 7.5 L of zero air at  $1 \text{ L min}^{-1}$ , each diluted liquid standard was injected using a Hamilton syringe (Restek Corporation). Care was taken to ensure rapid liquid volatilization by gently agitating the Tedlar bag while the drop hung at the end of the syringe needle. Once

all standards were added and volatilized, the remaining 2.5 L of zero air was added to help ensure adequate mixing. The resulting gaseous mixture, with a concentration range of 1–150 ppb for each compound, was analyzed by PTR-MS on the first and last day of each chamber period. All terpenes fragment onto  $m/z$  81 and 137, and sesquiterpenes were observed to fragment onto  $m/z$  149; therefore,  $m/z$  205 was the only parent mass not influenced by fragmentation. Because the standard mixture always included the entire suite of analytes (see Section 2.3.3.1), this calibration technique was only used for the primary sesquiterpene signal at  $m/z$  205.  $m/z$  149 was scaled to match the amount of methyl chavicol observed with the SPME fibers (see Section 2.3.3.1) knowing that  $m/z$  149 included minor contributions from sesquiterpene fragments.

### 2.3.2. GC-FID

Individual monoterpene species were separated and quantified from the branch emissions using GC-FID. Instrumentation details are found elsewhere (Lamanna and Goldstein, 1999), and sample processing and analysis is similar to that of Lee et al. (2005). To process the sample, the  $5 \text{ mL min}^{-1}$  subsample of air passed through a  $-10^\circ\text{C}$  cold trap to remove water vapor and through KI-coated glass wool to eliminate ozone. The sample was pre-concentrated in a 1/16 inch Silcosteel (Restek Corporation) tube packed with glass beads, Carboxen B (Sigma–Aldrich), and Tenax TA (Sigma–Aldrich). After 30 min of collection, the sample was heated from  $-10$  to  $220^\circ\text{C}$  within 20 s to desorb the trapped compounds into helium carrier gas and deliver them onto the head of a Rtx-5



**Fig. 2.** Schematic of branch enclosure setup.

(Restek Corporation) column. The inlet was manually cycled between measuring emissions from the chamber and the blank background zero air supply.

**2.3.2.1. Calibration.** The GC-FID was calibrated by diluting ppm-level monoterpene standards (described in Section 2.3.1.1) into a larger ( $1 \text{ L min}^{-1}$ ) flow of zero air. Monoterpene standards were used to check the identification of these compounds via their retention time and to determine an average response factor from the dominant compounds ( $\beta$ -pinene,  $\alpha$ -pinene, 3-carene, and limonene) which was applied for the quantification of all monoterpenes.

### 2.3.3. SPME fibers

Periodically, the branch enclosure was sampled with  $65 \mu\text{m}$  polydimethylsiloxane-divinylbenzene (PDMS/DVB) Stableflex fibers. SPME fibers provide an easy method for sampling the gas phase without requiring extraneous solvents or surfaces where compounds could be lost. The analytes are directly concentrated onto the fiber coating, then the fiber is placed into a GC injector port for thermal desorption (Pawliszyn, 1997). All fibers were transported on ice to a UC Berkeley laboratory and stored at  $<4^\circ\text{C}$  until analyzed using a Varian CP-3800 gas chromatograph with a Saturn 2200 ion trap mass spectrometer (GC-ITMS). A detailed description of the SPME method is presented by Bouvier-Brown et al. (2007).

**2.3.3.1. Calibration.** Tedlar bag standards (described in Section 2.3.1.1) were used to calibrate the SPME fibers. At the beginning and end of each one or two week sampling period, four fibers were exposed to four different Tedlar bags, each containing different concentrations of the BVOC standard mixture. A complete mixture of standards was used in each experiment so that any competitive preferences for the fiber coating would occur in every sample. Because the fibers were calibrated for methyl chavicol using an authentic standard, the concentration observed by SPME was used to scale  $m/z$  149 from the PTR-MS measurements.

### 2.4. Agreement between analytical techniques

There is good agreement between the monoterpene mixing ratios measured by PTR-MS and those measured by GC-FID (slope = 0.991,  $R^2 = 0.87$ ). The total amount of sesquiterpenes detected using PTR-MS also correlates well with the total amount of sesquiterpenes detected using SPME fibers (slope = 1.01,  $R^2 = 0.82$ ). Variability in the agreement of individual measurements of monoterpenes or sesquiterpenes is likely due to the presence of terpene species that have different responses than the standard mixtures in the instrumentation due to absorptive properties or fragmentation in the mass spectrometer. For example, there was a large variation in the mixture of emitted sesquiterpenes, but only  $\beta$ -caryophyllene was used for calibrating the fibers (Bouvier-Brown et al., 2007).

Methyl chavicol quantified with SPME fibers was used to scale the PTR-MS, but the two methods correlate in terms of temporal variations ( $R^2 = 0.87$ ). When using PTR-MS,

there is also small uncertainty in assigning one compound identity to one mass/charge ratio. The compound of interest likely fragments onto other unaccounted masses and the monitored mass may include fragments of larger compounds.

Periodic measurements of the zero air supply along with a diurnal cycle of the zero air-flowing through an empty chamber show insignificant amounts of analytes in blanks as compared to average concentrations detected in the enclosure during the entire experiment. The average sum of all monoterpenes in the empty chamber measured by GC-FID was  $0.31 \pm 0.14$  ppb (mean  $\pm$  SD). In contrast, the average sum of all monoterpenes measured by the GC-FID throughout the experiment was 3.18 ppb. The average mixing ratios from all blanks measured by PTR-MS were  $0.14 \pm 0.13$  ppb (total monoterpenes),  $0.08 \pm 0.11$  ppb (total sesquiterpenes), and  $0.07 \pm 0.15$  ppb (methyl chavicol), whereas the average mixing ratios during experiments were 3.6 ppb, 0.93 ppb, and 3.0 ppb, respectively. SPME fibers exposed to the blank chamber did not detect any trace of methyl chavicol or sesquiterpenes, while the average mixing ratios were 5.1 and 9.8 ppb for total sesquiterpenes and methyl chavicol, respectively during the experiment. Average concentrations measured by SPME fibers are understandably larger than mixing ratios measured by PTR-MS because the SPME technique was only used during daytime hours and the fibers are not susceptible to losses in tubing.

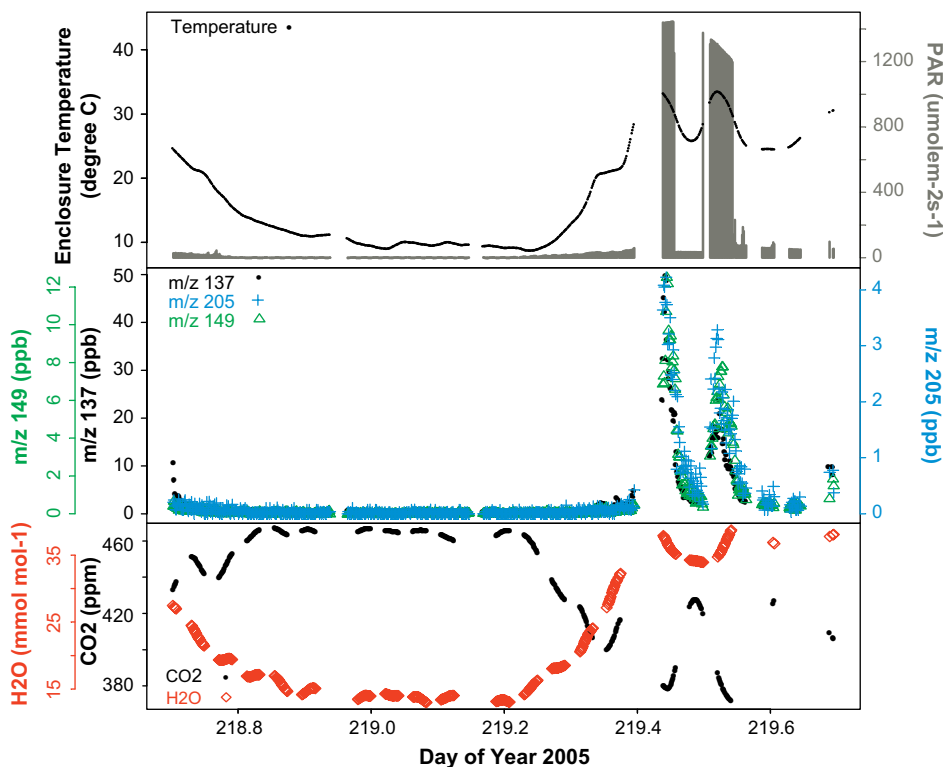
## 3. Results and discussion

### 3.1. Enclosure environment

The continuous measurements of PAR, temperature,  $\text{H}_2\text{O}$  vapor, and  $\text{CO}_2$  along with the parent analyte ions ( $m/z$  137, 149, 205) are illustrated in Fig. 3 for Pp pine branch #2 during the August sampling period. The enclosure temperature was within range of temperatures normally encountered in the ambient environment. Typical ambient  $\text{CO}_2$  concentrations are  $\sim 380$  ppm, so the amount of  $\text{CO}_2$  in the enclosure is slightly different. During the day, the  $\text{CO}_2$  mixing ratio drops to below 375 ppm due to photosynthesis, and rises at night to above 450 ppm. This pattern is also mirrored in the water vapor concentration; during the day as the stomates open, it rises to above  $40 \text{ mmol mol}^{-1}$ , and at night it drops to  $\sim 15 \text{ mmol mol}^{-1}$ . As indicators of photosynthesis, the response of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  suggest that the branch is functioning normally and the addition of the enclosure did not significantly alter its physiology.

### 3.2. Emission profiles

The time series (Fig. 3) also illustrates how monoterpene, sesquiterpene, and methyl chavicol emissions all follow a diurnal pattern that reaches a midday maximum. We fit the PTR-MS data to the modeled exponential relationship suggested by Guenther et al. (1993),  $F(T) = F_{30} \exp(\beta(T-30))$ , where  $F_{30}$  is the basal emission rate at  $30^\circ\text{C}$  normalized by dried needle or leaf mass,  $T$  the temperature inside the enclosure, and  $\beta$  the temperature response factor (Table 1). When scaled with the ecosystem foliar density



**Fig. 3.** Time series of August Ppine #2 showing: PAR outside of the branch enclosure, temperature inside the enclosure, parent ions monitored ( $m/z$  137: monoterpenes,  $m/z$  149: methyl chavicol,  $m/z$  205: sesquiterpenes), and water and carbon dioxide mixing ratios inside the chamber. The sudden decrease in PAR and temperature inside the chamber is due to artificial shading.

(651 g(dry weight) $m^{-2}$ ), total monoterpene  $F_{30}$  values from previous studies at the site (Lee et al., 2005 and references therein) compare well with the average total monoterpene  $F_{30}$  from Ppine branch #1 ( $1.18 \pm 0.35 \mu\text{gC g(dry weight)}^{-1} \text{h}^{-1}$ ). The total monoterpene temperature response factors from all sampled species (average  $0.13 \pm 0.04 \text{ }^\circ\text{C}^{-1}$ ) compare well with previous reports from this site (Schade and Goldstein, 2003; Holzinger et al., 2006; Lee et al., 2005) and from other sites (Guenther et al., 1993; Helmig et al., 2006, 2007) considering that emissions are known to have both spatial and seasonal variability. Recent reports (Hansen and Seufert, 2003; Tarvainen et al., 2005; Helmig et al., 2006, 2007; Hakola et al., 2006) have shown sesquiterpenes with a slightly stronger temperature dependence than monoterpenes. The data presented here do not follow this pattern, and only the sesquiterpene values for Ppine branch #2 closely resemble the reported  $\beta$  ranges. The average Ppine branch #2 summer temperature dependence coefficients for monoterpenes ( $0.19 \pm 0.02 \text{ }^\circ\text{C}^{-1}$ ), sesquiterpenes ( $0.16 \pm 0.02 \text{ }^\circ\text{C}^{-1}$ ), and methyl chavicol ( $0.18 \pm 0.02 \text{ }^\circ\text{C}^{-1}$ ) are larger than any other Ppine branch. These  $\beta$  values are similar for all 3 terpene compound classes, whereas the other Ppine branches only show similarity between monoterpene and methyl chavicol temperature dependencies and the sesquiterpene dependence is smaller. To date, there are no published direct measurements of ambient sesquiterpene and methyl chavicol emission rates due to their low volatility and the high reactivity of many sesquiterpene species.

The modeled  $F_{30}$  and  $\beta$  values are a lower estimation because the model poorly captured the high flux data points. This suggests that there are parameters in addition to temperature that significantly impact emissions, such as light, moisture, insect behavior, etc. Light is likely the dominant additional factor. Fitting the data to the isoprene emission model described by Guenther et al. (1993), where emissions are dependent on both light and temperature, and using the temperature dependence coefficients noted in Table 1, explains an average of 3, 22, and 10% of the monoterpene, methyl chavicol, and sesquiterpene variability, respectively, at high temperatures. However, no controlled experiments were executed to assess the light dependence parameters at constant temperatures, so they are not included here.

Although terpenes and methyl chavicol are very similar in origin and emission profiles, their oxidation can lead to different atmospheric results depending on the compound class. Thus it is important to look at the relative contribution of each class to the total emission profile. To do so, we averaged the observed fluxes over 30–34  $^\circ\text{C}$  for all branches except Ppine #1 in September where the 26–30  $^\circ\text{C}$  range was used due to lower ambient temperatures (Fig. 4).

### 3.3. Variation in emissions

#### 3.3.1. Monoterpenes

Monoterpenes were quantified using PTR-MS and GC-FID techniques. When averaging all data over the entire

**Table 1**

Modeled values for  $F_{30}$  and beta for each branch and each BVOC class measured (MT = monoterpenes, MC = methyl chavicol, and SQT = sesquiterpenes) using the  $F(T) = F_{30}\exp(\beta(T-30))$  algorithm.

	$F_{30}$ ( $\mu\text{g Cg}^{-1} \text{h}^{-1}$ )			Beta ( $^{\circ}\text{C}^{-1}$ )		
	MT	MC	SQT	MT	MC	SQT
<b>July</b>						
Ppine #1	0.781	1.090	0.054	0.131	0.155	0.047
Manzanita	0.217	n/a	0.197	0.077	n/a	0.059
Ceanothus	0.553	n/a	0.141	0.092	n/a	0.011
<b>August</b>						
Ppine #1	1.455	0.781	0.080	0.149	0.159	0.053
Ppine #2	0.892	0.159	0.410	0.209	0.196	0.151
Ppine #3	0.163	0.260	0.101	0.187	0.187	0.089
Manzanita	0.129	n/a	0.145	0.103	n/a	0.055
Ceanothus	0.537	n/a	0.164	0.128	n/a	0.026
<b>September</b>						
Ppine #1	1.294	0.347	0.553	0.133	0.136	0.101
Ppine #2	0.823	0.423	3.115	0.177	0.162	0.178
Ppine #3	0.185	0.375	0.316	0.118	0.122	0.076
Manzanita	0.161	n/a	0.160	0.112	n/a	0.027
All branches						
Average	0.599	0.491	0.453	0.133	0.160	0.073
$\pm$ SD	0.458	0.328	0.851	0.038	0.026	0.048
<b>Branch average</b>						
Ppine #1	1.177	0.739	0.229	0.138	0.150	0.067
$\pm$ SD	0.352	0.373	0.281	0.010	0.013	0.030
Ppine #2	0.858	0.291	1.763	0.193	0.179	0.164
$\pm$ SD	0.049	0.187	1.913	0.023	0.023	0.019
Ppine #3	0.174	0.318	0.209	0.153	0.154	0.083
$\pm$ SD	0.016	0.081	0.152	0.049	0.046	0.010
Manzanita	0.169	n/a	0.167	0.097	n/a	0.047
$\pm$ SD	0.044	n/a	0.030	0.018	n/a	0.020
Ceanothus	0.545	n/a	0.153	0.110	n/a	0.019
$\pm$ SD	0.011	n/a	0.020	0.026	n/a	0.010

time period, monoterpenes were the largest contributor to the observed emissions.

**3.3.1.1. Variation over time.** Total Ppine monoterpene basal emission rates within each branch remain relatively constant in August and September (Table 1). The monoterpene emission rate from Ppine branch #1 in July is considerably lower than in the other months. On the other hand, the temperature dependence coefficient ( $\beta$ ) for all Ppine branch emissions reaches a maximum in August. Manzanita's emission rate fluctuates slightly over the 3-month sampling period, with a minimum in August, while the emission rate from ceanothus stays constant. There is slight variation in the relative contribution of each monoterpene compound to the total emission over time within each branch. Using the GC-FID, 9 monoterpenes were separated; these included:  $\beta$ -pinene, 3-carene,  $\alpha$ -pinene, limonene (+ $\beta$ -phellandrene), camphene, myrcene,  $\alpha$ -terpinene, terpinolene, and  $\gamma$ -terpinene. In July, a large fraction of the total monoterpene flux emitted by both Ppine branch #1 and manzanita was myrcene, but for the rest of the summer, larger contributions are instead seen for  $\beta$ -pinene and  $\alpha$ -pinene, respectively (Fig. 5). Also, the contribution of  $\alpha$ -terpinene to the total monoterpenes emitted from Ppine branch #2 significantly increased from August to September (Fig. 5).

**3.3.1.2. Variation among branches.** The most significant differences occur between the different Ppine branches and

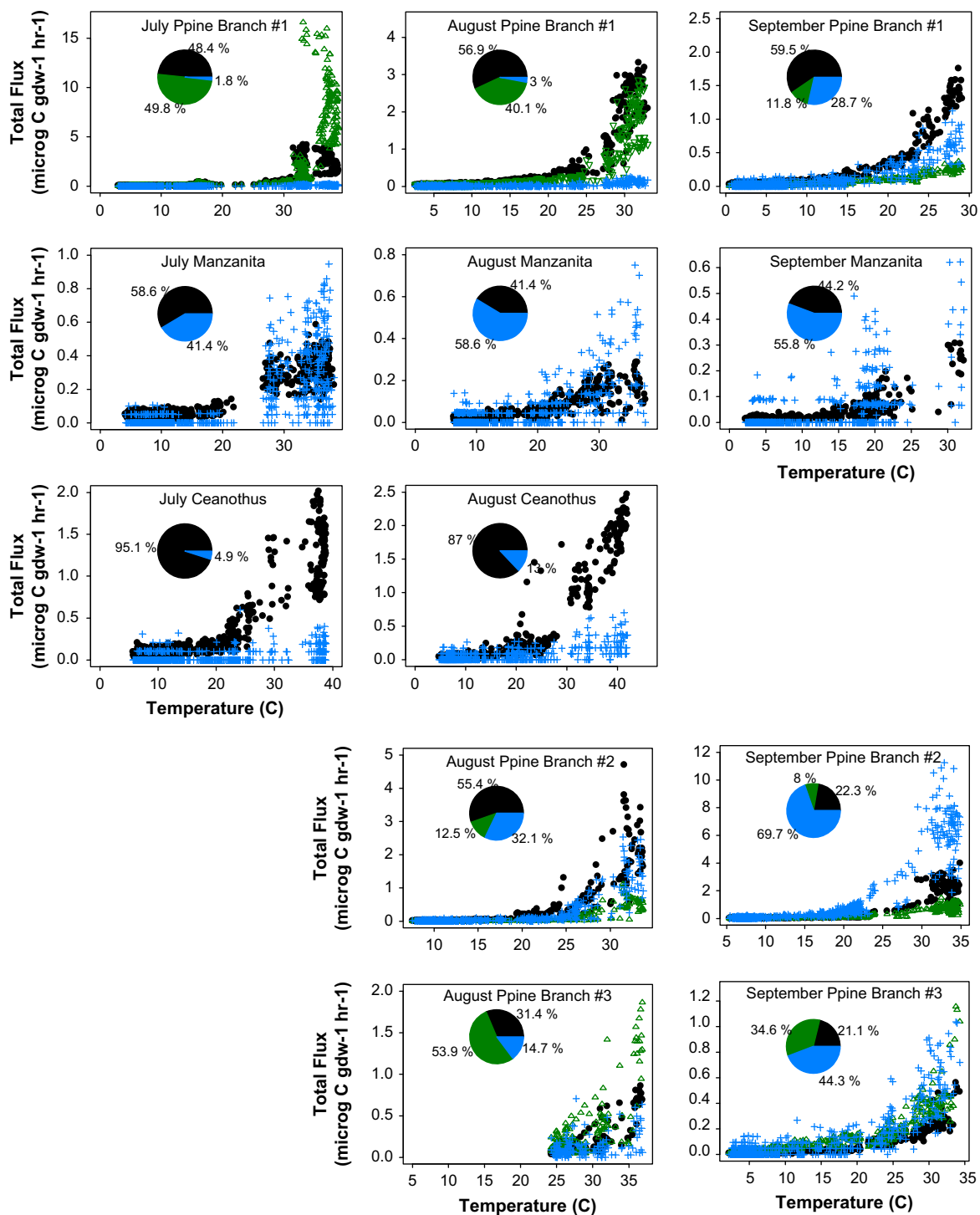
among the 3 species. Out of the 3 Ppine branches, Ppine branch #1 has the largest fraction of monoterpenes relative to the total terpene flux at any given time.  $\beta$ -pinene was the dominant monoterpene detected in Ppine branch #1 (52% daytime average) and branch #3 (40%), while 3-carene was dominant in Ppine branch #2 (35%). Ceanothus emissions significantly contribute to the total monoterpene flux at the site, and it was dominated by camphene (36%). Manzanita was mostly myrcene (35%), 3-carene (26%), or  $\alpha$ -pinene (25%) in July, August, and September, respectively, but its overall terpene flux had a relatively minor contribution to the site. The only unifying trend shows a decrease in myrcene in every branch of every plant species tested over the 3-month period. From July to August, myrcene emissions dropped by 285, 0.3, and 21% for Ppine branch #1, ceanothus, and manzanita, respectively. From August to September, these emissions decreased by 140, 5, and 6% for branches Ppine #1, manzanita, Ppine #2, and Ppine #3, respectively.

### 3.3.2. Sesquiterpenes

Sesquiterpenes were quantified using PTR-MS and SPME fiber techniques. Our data show that sesquiterpenes are an important contribution to the terpene flux at this site. Using two different quantitative methods, we detected larger emissions of sesquiterpenes than previously reported. In fact, averaging basal emissions from Ppine branches over the entire sampling time period, sesquiterpenes account for 83% of the monoterpene flux (see Table 1).

**3.3.2.1. Variation over time.** For each Ponderosa pine tree branch, the total sesquiterpene basal emission rate, the temperature dependence coefficient, and thus the sesquiterpene fraction of total terpene emission, significantly increased as the summer progressed (Table 1, Fig. 4). While the manzanita sesquiterpene basal emission rate fluctuated slightly over the 3 months, the emission rate from ceanothus remained steady. The manzanita temperature dependence coefficients remained stable between July and August, but decreased in September. The ceanothus coefficients increased from July to August.

**3.3.2.2. Variation among branches.** After sampling with SPME fibers, 26 different sesquiterpene compounds were detected, and 9 were identified by the MS library:  $\alpha$ -bergamotene (Ppine),  $\beta$ -farnesene (Ppine),  $\alpha$ -longipinene (Ppine),  $\alpha$ -cedrene (Ppine),  $\alpha$ -bisabolene (Ppine),  $\beta$ -cubebene (manzanita),  $\beta$ -caryophyllene (manzanita and ceanothus),  $\alpha$ -humulene (ceanothus), and  $\alpha$ -farnesene (all 3 plant species). The identified compounds account for 89% of the measured sesquiterpene mass from SPME fibers. There were 2–6 different compounds detected in every branch with the exceptions of Ppine branch #2 having 16 compounds in September and ceanothus not having any in July. Fig. 6 shows the branch-to-branch and monthly sesquiterpene variation as well as the agreement between PTR-MS and SPME fiber methods. The composition of sesquiterpene compounds slightly changed between branches and over time, but the quantity is greatest in September. The most important sesquiterpenes



**Fig. 4.** Emissions for all five branches sampled. • (black): Total monoterpenes, + (blue): Total sesquiterpenes, Δ (green): Methyl chavicol. The pie charts show the average contribution of each BVOC class (in the same color scheme) measured over a five-degree range where the flux maximizes (30–34 °C for all branches except September Ppne branch #1 where 26–30 °C was used). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article).

at this site were  $\alpha$ -bergamotene (79% of total Ppne sesquiterpene emissions),  $\alpha$ -farnesene (78% of total manzanita sesquiterpene emissions), and  $\beta$ -caryophyllene (73% of total ceanothus sesquiterpene emissions).

### 3.3.3. Methyl chavicol

Methyl chavicol emission from the Ppne trees was observed and quantified by PTR-MS and SPME fiber analyses. Methyl chavicol accounted for 8–54% of the total

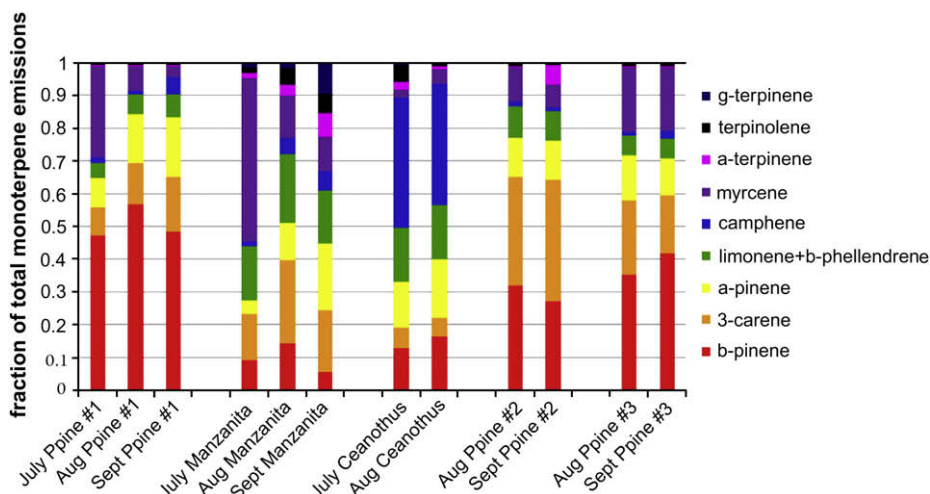


Fig. 5. Fractional contribution of each monoterpene to the total monoterpene emissions from each branch.

terpene + methyl chavicol emissions from individual Ppine branches (Fig. 4), and thus our data suggests that it can be a dominant emission from Ppine. Methyl chavicol was first identified in ambient air using PTR-MS (Holzinger et al., 2005); however, there is no published report of its emission rate from any site. It is not surprising that methyl chavicol emissions are detectable; studies of Ppine oil composition show methyl chavicol comprising 3–40% of the total needle oil (Zavarin et al., 1971), an amount comparable to that of 3-carene (Krauze-Baranowska et al., 2002).

3.3.3.1. *Variation over time.* Our data show a decrease in the contribution of methyl chavicol to the total terpene + methyl chavicol flux from all Ppine branches as the summer progresses (Fig. 4). The absolute emission rate for all Ppine branches does not show a strong trend because while the basal emission rate for Ppine branch #1 reaches a minimum in September, Ppine branches #2 and #3 reach a slight maximum in September (Table 1). The temperature coefficient ( $\beta$ ) for all Ppine branches maximizes in August (Table 1).

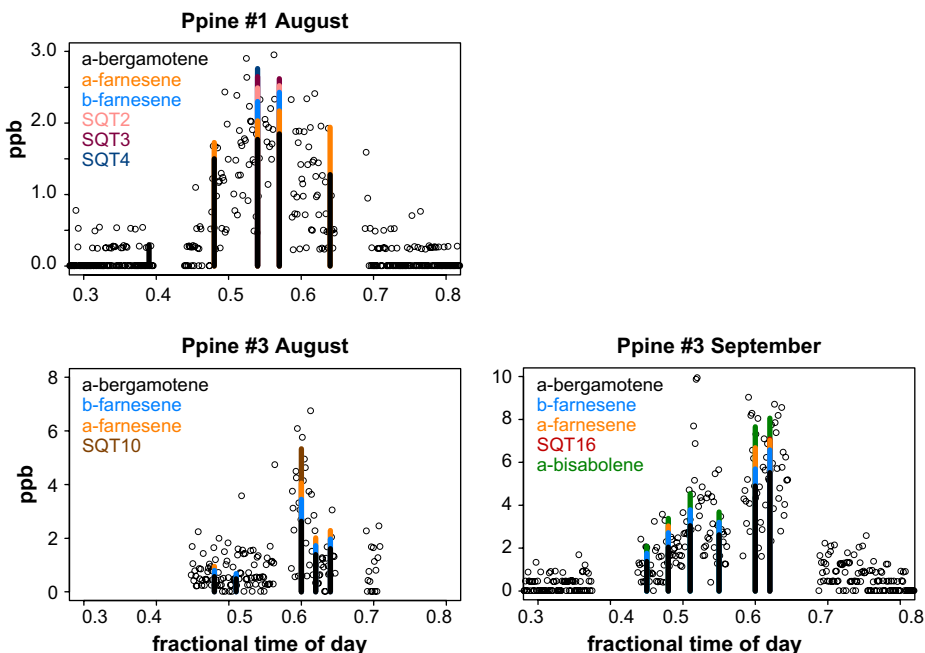


Fig. 6. The PTR-MS data is shown as open circles, and SPME data are the bars broken into the individual sesquiterpene compounds quantified.



### 3.3.4. Emission variation

The data presented here show a relatively constant monoterpene emission rate, an increase in sesquiterpene emissions, and a decrease in the methyl chavicol contribution to emissions throughout the summer (Fig. 4). Monoterpene basal emissions have been shown to reach a maximum during the warm growing season (spring and summer) and minimize in autumn and winter in numerous chamber studies of various pine species around the world (e.g. Staudt et al., 2000; Kim et al., 2005). However, many studies have also shown a secondary increase in emissions in late summer or autumn (Komenda and Koppmann, 2002; Pressley et al., 2004; Tarvainen et al., 2005; Hakola et al., 2006). Pressley et al. (2004) noticed this trend only in branches growing low in the canopy. While Komenda and Koppmann (2002) suggest this secondary increase was a biological reaction to stress caused by unseen pathogen or herbivore damage, Hakola et al. (2006) attribute the emission increase in autumn to the growth of new needles. Since many terpenes are emitted through similar mechanisms and if monoterpene emissions can increase late in the growing season, it is reasonable to suppose that sesquiterpenes could also be emitted in larger quantities in late summer or early autumn as shown by our data (Table 1, Fig. 4). However, it is impossible to show a definitive seasonal trend for the compounds measured in this study because they were only monitored for 3 consecutive months.

There have been very few studies looking at the seasonal trends of sesquiterpenes. While three different experiments sampled emissions from Scots pine trees, the time at which sesquiterpene emissions reach a maximum seems to vary between sites. In Hyytiälä, Finland, sesquiterpene emissions were only observed in the summer where they peaked in July (Hakola et al., 2006), whereas in the previous year, due to inconclusive results in late summer, sesquiterpenes were only observed in the summer and autumn at equal amounts (Tarvainen et al., 2005). At Sodankylä, Finland, the emissions were still increasing from April to May to June (Tarvainen et al., 2005), thus a maximum was not reached. In Freiburg, Germany, the highest sesquiterpene emissions were measured in late spring/early summer and continued to decrease into autumn (Holzke et al., 2006). Helmig et al. (2007) reported that the mixture of sesquiterpenes emitted from loblolly pine differed between two successive years. They suggested that it is either due to seasonal or year-to-year changes or inter-tree variability within the same species.

### 3.3.5. Inter-tree variability

There are clear differences in terpene emission rates and composition between the different Ponderosa pine branches. The three branches sampled in this experiment were each on different trees, so it is unclear if the variability observed is due to inter-branch or inter-tree differences, although plant-to-plant variability has been shown to be larger (Komenda and Koppmann, 2002). The trees were all within 10–15 m of each other, sharing the same soil and water characteristics. While every branch sampled was sunlit for a large portion of the day, Ppine branch #1 and #3 mainly received afternoon and evening sun while Ppine

branch #2 received the morning and afternoon sun. It is not unusual to see an array of variability both in absolute amount and relative monoterpene emission composition between trees (Staudt et al., 2001; Komenda and Koppmann, 2002; Komenda et al., 2003; Holzke et al., 2006). The difference in emissions may be due to differing enzymes and/or enzyme activity (Komenda and Koppmann, 2002). Since enzyme presence and activity are genetically controlled, it is likely that the interspecies variability is genetic. From the analysis of Ppine xylem resin from trees throughout Arizona and Colorado, Latta et al. (2003) could assign each individual Ppine tree to one of 5 characteristic chemotypes. One chemotype, noted by dominant amounts of  $\beta$ -pinene and 3-carene and a minor contribution from  $\alpha$ -pinene, is very similar to the emission profile of Ppine branch #2. In summary, the variation seen between the different Ppine branches did not exceed what can be explained by inter-tree variability.

### 3.4. Missing primary terpenes

In this branch enclosure study, we offer evidence that helps account for some of the missing biogenic precursors necessary to explain previous observations at the Blodgett forest site. Chemical ozone loss dominates the ozone flux at this site, and since it scales with temperature, the loss is likely due to reactions with BVOCs emitted in a similar manner as terpenes (Kurpius and Goldstein, 2003). The estimated amount of terpene-like compounds responsible for the summer daytime average  $20 \mu\text{mol m}^{-2} \text{h}^{-1}$  observed chemical ozone flux is approximately 10 (6–13) times more than the amount of monoterpene emissions measured above the canopy (Goldstein et al., 2004). In a subsequent study, Holzinger et al. (2005) estimated the need for 6–30 times the emission of total monoterpenes to attain the amount of oxidation products observed in and above the forest canopy. Reactive nitrogen at this site has provided further evidence for unaccounted BVOC emissions. Farmer and Cohen (2008) measured a surprising summertime upward flux of  $\text{HNO}_3$  and attribute the high mixing ratio of OH needed to produce  $\text{HNO}_3$  to the ozonolysis of terpenes. All of these studies suggest gaps in our knowledge of within canopy chemistry that could be explained by additional BVOC emissions.

To assess whether our branch level measurements of sesquiterpene and methyl chavicol emissions could account for the observed ozone chemical flux, we first compiled the oxidation rates for all quantified analytes (Table 2). Rate constants not found in the literature were calculated based on chemical structure using the Environmental Protection Agency's Estimation Program Interface Suite (US EPA AOP-WIN, 2000). Using estimates introduces uncertainty in the rate constants, particularly  $k_{\text{O}_3}$ . For example, the EPA estimate for  $\beta$ -caryophyllene and  $\alpha$ -humulene is 27 and 13 times slower than the literature values, respectively, but the estimate for longifolene is 23 times faster than the literature value. Average basal emission rates and reaction rates were calculated for monoterpenes, sesquiterpenes, and methyl chavicol by scaling the rates to the average fractional contribution from each compound and the 2003 percent leaf area contribution to the ecosystem for each plant species

**Table 2**

Structures and reactivity for all analytes identified and quantified in the branch enclosures.

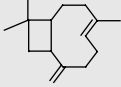
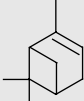
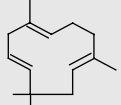

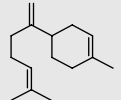
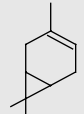
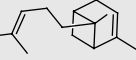
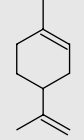
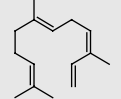
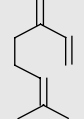
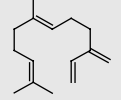

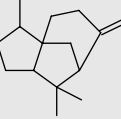
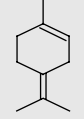
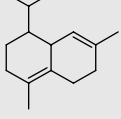
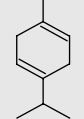
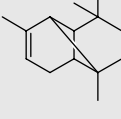
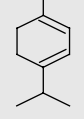
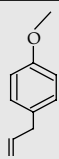
Compound	Structure	$k_{OH}^a$	$\tau_{OH}^c$	Compound	Structure	$k_{OH}^a$	$\tau_{OH}^c$
		$k_{O_3}^a$	$\tau_{O_3}^d$			$k_{O_3}^a$	$\tau_{O_3}^d$
		$k_{NO_3}^a$	$\tau_{NO_3}^e$			$k_{NO_3}^a$	$\tau_{NO_3}^e$
		( $cm^3\ molec^{-1}\ s^{-1}$ )	(min)			( $cm^3\ molec^{-1}\ s^{-1}$ )	(min)
$\beta$ -Caryophyllene (C <sub>15</sub> H <sub>24</sub> )		$2.0 \times 10^{-10}$	15.4	$\alpha$ -Pinene (C <sub>10</sub> H <sub>16</sub> )		$5.3 \times 10^{-11}$	58.2
		$1.2 \times 10^{-14}$	0.93			$8.4 \times 10^{-17}$	132
		$2.2 \times 10^{-11}$	13.6			$6.1 \times 10^{-12}$	49
$\alpha$ -Humulene (C <sub>15</sub> H <sub>24</sub> )		$3.0 \times 10^{-10}$	10.3	$\beta$ -Pinene (C <sub>10</sub> H <sub>16</sub> )		$7.7 \times 10^{-11}$	40.1
		$1.2 \times 10^{-14}$	0.93			$1.5 \times 10^{-17}$	741
		$3.3 \times 10^{-11}$	9.07			$2.5 \times 10^{-12}$	120
$\alpha$ -Bisabolene (C <sub>15</sub> H <sub>24</sub> )		$2.3 \times 10^{-10b}$	13.4	3-Carene (C <sub>10</sub> H <sub>16</sub> )		$8.7 \times 10^{-11}$	35.5
		$8.7 \times 10^{-16b}$	12.8			$3.7 \times 10^{-17}$	300
		?				$9.5 \times 10^{-12}$	31.5
$\alpha$ -Bergamotene (C <sub>15</sub> H <sub>24</sub> )		$1.8 \times 10^{-10b}$	17.1	Limonene (C <sub>10</sub> H <sub>16</sub> )		$1.7 \times 10^{-10}$	18.2
		$8.6 \times 10^{-16b}$	12.9			$2.0 \times 10^{-16}$	55.6
		?				$1.3 \times 10^{-11}$	23
$\alpha$ -Farnesene (C <sub>15</sub> H <sub>24</sub> )		$3.2 \times 10^{-10b}$	9.6	Myrcene (C <sub>10</sub> H <sub>16</sub> )		$2.1 \times 10^{-10}$	14.7
		$1.0 \times 10^{-15b}$	11.1			$4.7 \times 10^{-16}$	23.6
		?				$1.1 \times 10^{-11}$	27.2
$\beta$ -Farnesene (C <sub>15</sub> H <sub>24</sub> )		$2.8 \times 10^{-10b}$	11.0	Camphene (C <sub>10</sub> H <sub>16</sub> )		$5.34 \times 10^{-11}$	57.8
		$8.7 \times 10^{-16b}$	12.8			$9.19 \times 10^{-19}$	12,090
		?				$6.54 \times 10^{-13}$	458
$\alpha$ -Cedrene (C <sub>15</sub> H <sub>24</sub> )		$6.2 \times 10^{-11b}$	49.8	Terpinolene (C <sub>10</sub> H <sub>16</sub> )		$2.3 \times 10^{-10}$	13.4
		$1.2 \times 10^{-17b}$	926			$1.9 \times 10^{-15}$	5.8
		?				$9.5 \times 10^{-11}$	3.1
$\beta$ -Cubebene (C <sub>15</sub> H <sub>24</sub> )		$2.1 \times 10^{-10b}$	14.7	$\gamma$ -Terpinene (C <sub>10</sub> H <sub>16</sub> )		$1.8 \times 10^{-10}$	17.1
		$1.6 \times 10^{-15b}$	6.9			$1.4 \times 10^{-16}$	79.4
		?				$3.3 \times 10^{-11}$	9.1
$\alpha$ -Longipinene (C <sub>15</sub> H <sub>24</sub> )		$9.6 \times 10^{-11b}$	32.2	$\alpha$ -Terpinene (C <sub>10</sub> H <sub>16</sub> )		$3.6 \times 10^{-10}$	8.6
		$4.3 \times 10^{-16b}$	25.8			$2.1 \times 10^{-14}$	0.53
		?				$1.3 \times 10^{-10}$	2.3

Table 2 (continued)

Compound	Structure	$k_{\text{OH}}^{\text{a}}$	$\tau_{\text{OH}}^{\text{c}}$	Compound	Structure	$k_{\text{OH}}^{\text{a}}$	$\tau_{\text{OH}}^{\text{c}}$
		$k_{\text{O}_3}^{\text{a}}$	$\tau_{\text{O}_3}^{\text{d}}$			$k_{\text{O}_3}^{\text{a}}$	$\tau_{\text{O}_3}^{\text{d}}$
		$k_{\text{NO}_3}^{\text{a}}$	$\tau_{\text{NO}_3}^{\text{e}}$			$k_{\text{NO}_3}^{\text{a}}$	$\tau_{\text{NO}_3}^{\text{e}}$
		( $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ )	(min)			( $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ )	(min)
				Methyl chavicol ( $\text{C}_{10}\text{H}_{12}\text{O}$ )		$5.4 \times 10^{-11\text{b}}$ $1.2 \times 10^{-17\text{b}}$ ?	57.2 925.9

<sup>a</sup> Reaction rates from Atkinson and Arey (2003), except where noted.

<sup>b</sup> Reaction rates estimated from Environmental Protection Agency's Estimation Program Interface Suite (US EPA AOPWIN, 2000).

<sup>c</sup> Assuming average daytime oxidant mixing ratios:  $[\text{OH}] = 5.4 \times 10^6 \text{ molec cm}^{-3}$  (0.25 ppt) (W. Brune, J. Mao, pers. comm.).

<sup>d</sup> Assuming average daytime oxidant mixing ratios:  $[\text{O}_3] = 1.5 \times 10^{12} \text{ molec cm}^{-3}$  (70 ppb).

<sup>e</sup> Assuming average daytime oxidant mixing ratios:  $[\text{NO}_3] = 5.6 \times 10^7 \text{ molec cm}^{-3}$  (2.6 ppt) (C. Minejima, pers. comm.).

Table 3

Monoterpene, sesquiterpene, and methyl chavicol contribution to chemical ozone flux.

	Emissions $\mu\text{mol m}^{-2} \text{ h}^{-1}$	$k_{\text{O}_3}$ $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	$\tau_{\text{O}_3}$ min	Percent lost ( $\text{O}_3$ ) 1, 10 min	$\text{O}_3$ flux <sub>chem</sub> $\mu\text{mol m}^{-2} \text{ h}^{-1}$ 1, 10 min	$k_{\text{OH}} \text{ cm}^3$ $\text{molec}^{-1} \text{ s}^{-1}$	$\tau_{\text{OH}}$ min	Percent lost (OH) 1, 10 min
Monoterpenes	3.08	$6.9 \times 10^{-16}$	16.1	6.2, 62%	0.191, 1.91	$1.1 \times 10^{-10}$	27.6	3.6, 36%
Sesquiterpenes	1.51	$3.3 \times 10^{-15}$	3.4	30, 100%	0.453, 1.51	$2.2 \times 10^{-10}$	14.0	7.1, 71%
Methyl chavicol	1.37	$1.2 \times 10^{-17}$	926	0.11, 1.1%	0.002, 0.015	$5.4 \times 10^{-11}$	55.1	1.9, 19%
Total (1:1 BVOC + $\text{O}_3$ stoichiometry)					0.646, 3.44			
Total (2:1 sesquiterpene + $\text{O}_3$ stoichiometry, 1:1 for other BVOCs)					1.10, 4.95			

Average basal emission rates and reaction rates were calculated for each BVOC class by scaling the rates to the average fractional contribution from each compound and the percent leaf area contribution to the ecosystem for each plant species. Emissions were also scaled with the ecosystem foliar density.

(52% Pine, 29% manzanita, 19% ceanothus). Emissions were also scaled with the ecosystem foliar density. Lifetimes of monoterpenes, sesquiterpenes, and methyl chavicol were then calculated (Table 3) using average daytime oxidant mixing ratios:  $[\text{O}_3] = 1.5 \times 10^{12} \text{ molec cm}^{-3}$  (70 ppb) and  $[\text{OH}] = 5.4 \times 10^6 \text{ molec cm}^{-3}$  (0.25 ppt) (W. Brune, J. Mao, pers. comm.). The percent loss of each BVOC class via reaction with ozone or OH is estimated considering a canopy residence time of 1 or 10 min (Kurpius and Goldstein, 2003; Holzinger et al., 2005; Farmer and Cohen, 2008). For this analysis we assume a monoterpene or methyl chavicol molecule destroys 1 ozone molecule whereas a sesquiterpene destroys 1 or 2  $\text{O}_3$  molecules (more than one  $\text{O}_3$  molecule could react with a sesquiterpene due to multiple carbon-carbon double bonds). These BVOCs together account for a total of 3.2% (0.646/20) to 25% (4.95/20) of the chemical ozone flux estimated by Kurpius and Goldstein (2003). For comparison, each compound class's lifetime and percent loss to OH is also included in Table 3. Terpene oxidation is dominated by reaction with  $\text{O}_3$ , especially for sesquiterpenes. An additional 5–15% of the chemical ozone flux is likely due to reaction with NO from soil and plants (Kurpius and Goldstein, 2003), and assuming an ecosystem flux of  $2 \text{ mgC m}^{-2} \text{ h}^{-1}$  as measured by Schade et al. (2000), 2-methyl-3-buten-2-ol (MBO) will contribute another 0.14–1.4%, depending on the canopy residence time. This analysis accounts for 8.3–41% of the ozone flux due to chemistry,

which is a significant fraction, but does not completely explain the observed  $\text{O}_3$  loss at Blodgett forest. Some uncertainties remain regarding the sesquiterpene reaction mechanisms and oxidation rates, and potential soil emissions that could also react with  $\text{O}_3$ . Also, any reactive BVOC with similar adsorption properties as monoterpenes would not have been detected using SPME fibers (Bouvier-Brown et al., 2007) in the branch enclosure emission studies. However, the lack of closure for the chemical  $\text{O}_3$  flux based on our analysis suggests there could still be significant additional emissions of unmeasured BVOCs such as diterpenes, homoterpenes, and oxygenated sesquiterpenes from this forest ecosystem.

#### 4. Conclusions

By quantifying monoterpene, sesquiterpene, and methyl chavicol emissions from Ponderosa pine, manzanita, and ceanothus branches using branch enclosures, we clearly show that sesquiterpene and methyl chavicol emissions are important contributors to the overall terpene + methyl chavicol flux at this site. Using both PTR-MS and SPME fiber methods, we measured more methyl chavicol and total sesquiterpenes throughout the three months than have been reported previously. In the Pine samples, the sesquiterpene basal emission and temperature dependence (and thus fraction of total terpene + methyl chavicol

emission) increased from July to September. The contribution from methyl chavicol declined as the summer progressed. There were large variations of each terpene class among the different plant species and between the different Pp pine branches. Emissions of total and speciated terpenes also varied over the 3-month sampling period. The BVOC emissions quantified in this study readily react with ozone, significantly impacting the chemical ozone flux at Blodgett forest and forming oxidation products that likely contribute to SOA loading. Based on their significance at this site, we argue that sesquiterpenes and methyl chavicol must be included in biogenic emission models as input to atmospheric chemistry and SOA models.

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